Indian J. Phys. **52B**, 326–335 (1978)

Phase shift differences for some trigonometrical potentials

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(*Received* 28 *July* 1977, *revised* 27 *January* 1978 *and* 10 *May* 1978)

Using the semi-empirical relations established by Tietz phase shift differences for the radial Schrödinger wave equation have been evaluated for three different trigonometrical potential energy functions viz., the Rosen-Morse, Poschl-Teller and Clinton-Frattali potentials. It has been observed that the two together, with the knowledge of a particular phase shift enable one to determine the value of any other phase shift whatsoever.

1. INTRODUCTION

The most direct information about the interaction of particles in a diatomic molecule is obtained from the study of molecular scattering. To describe such a scattering one generally requires to solve the Schrödinger equation

$$\left[\frac{-\hbar^2}{2m}\nabla^2+V(r)\right]\psi = E\psi. \qquad \ldots (1)$$

In spherical co-ordinates the Laplacian operator ∇^2 is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}L^2(\theta,\phi), \qquad \ldots (2)$$

where

$$L^2(\theta,\phi) = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \qquad \ldots (3)$$

L is the orbital angular momentum operator. The wavefunction $\psi = \psi(r, \theta, \phi)$ may be written as

$$\psi = r^{-1}u_l(r)Y_{lm}(\theta,\phi), \qquad \ldots (4)$$

$u_l(r)$ is the radial part of the wavefunction ψ, and $Y_{lm}(\theta, \phi)$ the spherical harmonics with properties

$$L^2Y_{lm}(\theta,\phi) = l(l+1)\hbar^2Y_{lm}(\theta,\phi) \qquad \ldots (5)$$

$$L_zY_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi). \qquad \ldots (6)$$

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In eqs. (5) and (6) l and m are respectively the orbital angular momentum quantum number and the magnetic quantum number.

If ψ of eq. (4) is now substituted in eq. (1) we get after some manipulation the radial part of the wave equation as

$$\frac{d^2u_l}{dr^2}+\left[k^2-U(r)-\frac{l(l+1)}{r^2}\right]u_l = 0 \qquad \ldots (7)$$

In eq. (7) $k^2 = 2ME/\hbar^2$, $U(r) = 2MV(r)/\hbar^2$, M is the reduced mass of the interacting particles and $V(r)$ their potential energy. E is the relative kinetic energy.

The potential energy $V(r)$ should be such that it vanishes sufficiently rapidly with increasing r, and may be neglected beyond some radius, say $r = R$.

The wavefunction $u_l(r)$ should also vanish at the origin. This boundary condition at the origin follows from the requirement that the wavefunctions $\psi(r)$ and its gradient be finite everywhere.

Beyond the range of the potential i.e., for $r > R$ the wavefunction $v_l(r)$ will be obtained from the solution of the equation

$$\frac{d^2v_l}{dr^2}+\left[k^2-\frac{l(l+1)}{r^2}\right]v_l = 0. \qquad \ldots (8)$$

The difference in phase between the two waves $u_l(r)$ and $v_l(r)$ gives the phase-shift η_l corresponding to the potential $V(r)$. Exact analytical calculation of η_l from the above equations is extremely difficult, particularly for potential having a more complicated form. Munn *et al* (1964) accurately determined the value of η_l for the Lennard-Jones potential. But the method involves tedious numerical calculations and gives no analytical form for the solution. Among others, a semiempirical method due to Tietz (1963) seems to be simple and suitable particularly for the complicated potentials. Rather than giving individual η_l it gives a difference like $\eta_l-\eta_{l+1}$ or $\eta_{l-1}-\eta_{l+1}$:

$$\eta_l-\eta_{l+1} = \frac{\pi}{2k}\int_0^\infty r\,\frac{dU(r)}{dr}\,J_{l+1/2}(kr)J_{l+3/2}(kr)dr \qquad \ldots (9)$$

and

$$\eta_{l-1}-\eta_{l+1} = \frac{(l+1/2)\pi}{k^2}\int_0^\infty \frac{dU(r)}{dr}\,J^2{}_{l+1/2}(kr)dr. \qquad \ldots (10)$$

It is interesting to note that these relations (eqs. (9) and (10)) can analytically express the difference between the two continuous phase-shifts partly as the

radial rate of change of the potential and partly as the product of two Bessel functions. In the present paper our aim is to use these relations to determine phase shift differences for various potential functions.

In the study the potential $V(r)$ which represents the interaction between the scattered particle and the scatterer, should decrease in magnitude as the distance from the scattering centre becomes large. Such an accurate potential is provided by the all electron non-empirical quantum mechanical calculations (Schaefer 1972) or by the Rydberg-Klein-Rees (Rydberg 1931, 1933; Klein 1932; Rees 1947) method. Though these methods are unbiased, systematic and accurate, give only numerical values of the potential at a series of points. However, for all practical purposes one needs a suitable analytical expression for the same. With this view, a large number of semi-empirical potentials (Morse 1929; Rosen & Morse 1932; Pöschl & Teller 1933; Lippincott 1955, 1953; Varshni 1957) have been proposed from time to time. Varshni (1957) and Steele *et al* (1962), in their pioneering reviews, have given critical discussions of a large number of semi-empirical potentials for systems where chemical interactions are operative. Among these, the potentials of Rosen & Morse (1932), Poschl & Teller (1933) and of Clinton & Frattali (1960, 1963) are found to be fairly well. Our aim in this investigation is to employ these three trigonometrical potentials to the evaluation of phase shift differences (using relations (9) and (10)).

2. Derivation of Expressions for Phase Shifts

A. *Rosen-Morse Potential*

Rosen and Morse, in connection with the study of vibrations in polyatomic molecules, have proposed the potential

$$V(r) = A \tanh (r/d) - B \operatorname{sech}^2(r/d) \qquad \ldots \quad (11a)$$

where

$$\tanh (r_e/d) = -A/2B$$

$$D_e = (A+2B)^2/4B$$

$$k_e = (4B^2-A^2)/8d^2B^3$$

$$\text{and } (k_e/2D_e) = [1+\tanh (r_e/d)]^2/d^2. \qquad \ldots \quad (11b)$$

$-D_e$ is the minimum value of the potential energy, r_e is the value of r at which $V(r) = -D_e$ and k_e is the vibrational force constant around $r = r_e$. Steele *et al* (1962) have shown that this three-parameter potential predicts $(V_{RKR}-V(r))/D_e$ within 3·71%, α_e within 22·33% and $\omega_e x_e$ within 21·24% for the nineteen different states of eight molecules studied. Thus, this potential, in spite of having slightly more complicated form, appears to give better prediction of the spectroscopic constants and better reproduction of *RKR* curves than the more widely used Morse potential function.

To determine the above phase-shift differences let us first evaluate the following general integrals :

$$\int_0^\infty r^\lambda \operatorname{sech}^2(r/d) J_\mu(kr) J_\nu(kr)\,dr = 2S(\mu,\nu,\lambda) \sum_{n=0}^{\infty} (-1)^n \frac{k^{\mu+\nu} d^{\mu+\nu+\lambda+1}}{(n+1)^{\mu+\nu+\lambda}}$$

$$F\left(\frac{\mu+\nu+\lambda+2}{2}, \frac{\mu+\nu+\lambda+1}{2}, \frac{\mu+\nu+2}{2}, \frac{\mu+\nu+1}{2}; \mu+1, \nu+1,\right.$$

$$\left.\mu+\nu+1; -\left(\frac{kd}{n+1}\right)^2\right) \qquad \ldots (12)$$

where

$$S(\mu,\nu,\lambda) = \frac{\Gamma\left(\frac{\mu+\nu+\lambda+2}{2}\right)\Gamma\left(\frac{\mu+\nu+\lambda+1}{2}\right)\Gamma\left(\frac{\mu+\nu+2}{2}\right)\Gamma\left(\frac{\mu+\nu+1}{2}\right)}{\pi\Gamma(\mu+\nu+1)\,\Gamma(\mu+1)\,\Gamma(\nu+1)} \qquad \ldots (13)$$

$$\int_0^\infty r^\lambda \operatorname{sech}^2(r/d) \tanh(r/d)\, J_\mu(kr) J_\nu(kr)\,dr$$

$$= 2S(\mu,\nu,\lambda) \sum_{n=0}^{\infty} (-1)^n \frac{k^{\mu+\nu} d^{\mu+\nu+\lambda+1}}{(n+1)^{\mu+\nu+\lambda-1}} \cdot$$

$$F\left(\frac{\mu+\nu+\lambda+2}{2}, \frac{\mu+\nu+\lambda+1}{2}, \frac{\mu+\nu+2}{2}, \frac{\mu+\nu+1}{2};\right.$$

$$\left.\mu+1, \nu+1, \mu+\nu+1; -\left(\frac{kd}{n+1}\right)^2\right). \qquad \ldots (14)$$

For the evaluation of these integrals we have used the series expansion of (Gradshtyn & Ryzhik 1965) $\operatorname{sech}^2 x$ and $\operatorname{sech}^2 x \tanh x$.

Now substituting $dU(r)/dr$ in eq. (9) and evaluating the resulting expression with the help of above integrals (eqs. (13) and (14) with $\mu = l+1/2$, $\nu = l+3/2$ and $\lambda = 1$) we get

$$\eta_l - \eta_{l+1} = k^{2l+1} d^{2l+3} \frac{\{\Gamma(l+2)\}^2}{\Gamma(2l+3)} \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)^{2l+2}} \left(\frac{A}{n+1} + 2B\right)$$

$$\times F(l+2, l+2; 2l+3; -\left(\frac{kd}{n+1}\right)^2). \qquad \ldots (15)$$

A similar substitution in eq. (10) but now with $\mu = \nu = l+1/2$ and $\lambda = 0$ gives

$$\eta_{l-1}-\eta_{l+1} = (2l+1)k^{2l-1}d^{2l+1}\ \frac{\{\Gamma(l+1)\}^2}{\Gamma(2l+2)}\ \sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1)^{2l}}\left(\frac{A}{n+1}+2B\right)$$

$$\times\ F\left(l+1, l+1; 2l+2; -\left(\frac{kd}{n+1}\right)^2\right). \qquad (16)$$

It is observed that the sum of $\eta_0-\eta_1$ and $\eta_1-\eta_2$ as calculated from eq. (15) is exactly the same as $\eta_0-\eta_2$ calculated from eq. (16). Thus provided η_0 is known we can calculate straight-forward η_1, η_2, η_3 etc. from the equations mentioned above.

B. *Clinton-Frattali Potential*

Using an exact adiabatic quantum mechanical method, Clinton and co-workers (1960, 1963) have solved in an indirect way, a second-order differential virial equation

$$r\frac{d^2V_p(r)}{dr^2} + 2\frac{dV_p(r)}{dr} + d\frac{<p|T|p>}{dr} = 0 \qquad \ldots\ (17)$$

where $V_p(r)$ is the potential energy of the p-th electronic state of a diatomic molecule with internuclear distance r, and $<p|T|p>$ is the expectation value of its corresponding electronic kinetic energy operator T. The solution results in an oscillatory potential function given by

$$V(r) = (A_1/r^v)\cos(w \ln r)+(A_2/r^v)\sin(w \ln r) \qquad \ldots\ (18)$$

where

$$\sigma^2 = r_e^2 k_e/D_e$$

$$-F = \frac{1}{3}\left[\frac{r_e(d^3V(r)/dr^3)}{(d^2V(r)/dr^2)}\right]_{r=r_e}+1$$

$$G = 15(F+1)^2 - r_e^2\left[\frac{(d^4V(r)/dr^4)}{d^2V(r)/dr^2}\right]_{r=r_e} \qquad \ldots\ (19)$$

$$v = 3/2F$$

$$w = \pm(\sigma^2-v^2)^{\frac{1}{2}}$$

$$A_1 = D_e r_e^v[(v/w)S-C]$$

$$A_2 = -D_e r_e^v[(v/w)C+S]$$

$$C = \cos(w \ln r_e)$$

and

$$S = \sin(w \ln r_e).$$

This is a four parameter oscillatory potential and has reasonable quantum mechanical basis. It is inferior only to the five parameter Hulburt-Hirschfelder (Hulburt & Hirschfelder 1941) potential. Its average performance has been shown to be much better than most of the well-known three parameter potentials viz., those of Morse (1929), Rydberg (1931, 1933), Varshni (1957), Lippincott (1953, 1955), Frost & Musulin (1954) etc.

In order to determine the phase shift differences we evaluate the following integrals :

$$\int_0 \cos(w \ln r) J_\mu(kr) J_\nu(kr) r^{-(v+t)} dr = [\xi_1 (k/2)^{v-wi+t} + \xi_2 (k/2)^{v+wi+t}]/(2k) \quad \ldots \quad (20)$$

and

$$\int_0 \sin(w \ln r) J_\mu(kr) J_\nu(kr) r^{-(v+t)} dr = -i[\xi_1 (k/2)^{v-wi+t} - \xi_2 (k/2)^{v+wi+t}]/(2k) \quad \ldots \quad (21)$$

where

$$\xi_1 = \frac{\Gamma(v-wi+t)\,\Gamma((v+\mu-v+wi+t+1)/2)}{\Gamma((-v+\mu+v-wi+t+1)/2)\,\Gamma((v+\mu+v-wi+t+1)/2)\,\Gamma((v-\mu+v+wi+t+1)/2)} \quad \ldots \quad (22)$$

$$\xi_2 = \frac{\Gamma(v+wi+t)\,\Gamma((v+\mu-v-wi-t+1)/2)}{\Gamma((-v+\mu+v+wi+t+1)/2)\,\Gamma((v+\mu+v+wi+t+1)/2)\,\Gamma((v-\mu+v+wi+t+1)/2)} \quad \ldots \quad (23)$$

where for the first terms of eqs. (20) and (21)

$$\mathrm{Re}(v+\mu+1) > \mathrm{Re}(v-wi+t) > 0, \qquad k > 0,$$

and for the second term

$$\mathrm{Re}(v+\mu+1) > \mathrm{Re}(v+wi+t) > 0, \qquad k > 0.$$

Then substituting the value of $dU(r)/dr$ in eq. (9) and evaluating the resulting integrals with the help of above equations (eqs. (20) and (21) with $\nu = l+1/2$, $\mu = l+3/2$ and $t = 0$) we get

$$\eta_l - \eta_{l+1} = \pi [w(A_2+iA_1) - v(A_1-iA_2)] \frac{k^{v-wi-2}}{2^{v-wi+2}}.$$

$$\times \frac{\Gamma(v-wi)\,\Gamma\left(\frac{2l-v+wi+3}{2}\right)}{\Gamma\left(\frac{v-wi}{v}\right)\Gamma\left(\frac{2l+v-wi+3}{2}\right)\Gamma\left(\frac{v-wi+2}{2}\right)}$$

$$+\pi[w(A_2-iA_1)-v(A_1+iA_2)]\,\frac{k^{v+wi-2}}{2^{v+wi+2}}\cdot$$

$$\times \frac{\Gamma(v+wi)\,\Gamma\left(\frac{2l-v-wi+3}{2}\right)}{\Gamma\left(\frac{v+wi}{2}\right)\Gamma\left(\frac{2l+v+wi+3}{2}\right)\Gamma\left(\frac{v+wi+2}{2}\right)} \qquad \ldots (24)$$

A similar substitution in eq. (10) but now with $\nu = \mu = l+1/2$ and $t = 1$ gives

$$\eta_{l-1}-\eta_{l+1} = (l+1/2)\pi[w(A_2+iA_1)-v(A_1-iA_2)]\,\frac{k^{v-wi-2}}{2^{v-wi+2}}\cdot$$

$$\frac{\Gamma(v-wi+1)\;\Gamma\left(\frac{2l-v+wi+1}{2}\right)}{\Gamma\left(\frac{v-wi+2}{2}\right)\Gamma\left(\frac{2l+v-wi+3}{2}\right)\Gamma\left(\frac{v-wi+2}{2}\right)}$$

$$+(l+1/2)\pi[w(A_2-iA_1)-v(A_1+iA_2)]\,\frac{k^{v+wi-2}}{2^{v+wi+2}}\cdot$$

$$\times \frac{\Gamma(v+wi+1)\;\Gamma\left(\frac{2l-v-wi+1}{2}\right)}{\Gamma\left(\frac{v+wi+2}{2}\right)\Gamma\left(\frac{2l+v+wi+3}{2}\right)\Gamma\left(\frac{v+wi+2}{2}\right)} \qquad \ldots (25)$$

It is found that the sum of $\eta_0-\eta_1$ and $\eta_1-\eta_2$ as calculated from eq. (24) is exactly the same as $\eta_0-\eta_2$ calculated from eq. (25). Thus eqs. (24) and (25) lead practically to the same approximate expression of the phase shifts.

3. *Pöschl-Teller Potential*

The function due to Pöschl & Teller (1933) has the form

$$V(r) = M\,\mathrm{cosech}^2(ar/2) - N\,\mathrm{sech}^2(ar/2) \qquad \ldots (26)$$

where

$$\tanh^4(ar_e/2) = M/N$$

$$a^2 = 32D_e/k_e$$

and

$$N = D_e/[1-\tanh^2(ar_e/2)]^2. \quad \ldots (27)$$

Davies (1949) examined this function on hydrogen halides and concluded from the values of $(d^3V(r)/dr^3)_{r=r_e}$ and $(d^4V(r)/dr^4)_{r=r_e}$ that it is slightly superior to the Morse function. Later Steele *et al* (1962), from a detailed comparative study, have concluded that this potentials is almost equivalent to the Morse, Rosen-Morse and Frost-Musulin potentials.

In order to determine phase shift differences in eqs. (26) and (27) let us first evaluate only the following general expression :

$$\int_0^\infty r^\lambda \operatorname{cosech}^2(ar/2)\coth(ar/2)J_\mu(kr)J_\nu(kr)dr. \quad \ldots (28)$$

A series expansion (Gradshteyn & Ryzhik 1965) substitution of $\operatorname{cosech}(ar/2)\cdot\coth(ar/2)$ in eq. (28) reduces the later to

$$2S(\mu,\nu,\lambda)\sum_{n=0}^{\infty}\frac{k^{\mu+\nu}(2/a)^{\mu+\nu+\lambda+1}}{(n+1)^{\mu+\nu+\lambda-1}}\cdot$$

$$\times F\left(\frac{\mu+\nu+\lambda+2}{2}, \frac{\mu+\nu+\lambda+1}{2}, \frac{\mu+\nu+2}{2}, \frac{\mu+\nu+1}{2};\right.$$

$$\left.\mu+1, \nu+1, \mu+\nu+1; -\left(\frac{2k}{a(n+1)}\right)^2\right). \quad \ldots (29)$$

Now substituting the value of $dU(r)/dr$ in eq. (9) and evaluating the resulting integrals with the help of above equations (eq. (14) with $\mu = l+1/2$, $\nu = l+3/2$, $\lambda = 1$ and $a = 2/d$, and eq. (29) with $\mu = l+1/2$, $\nu = l+3/2$ and $\lambda = 1$) we get

$$\eta_l-\eta_{l+1} = -\frac{2^{2l+4}k^{2l+1}}{a^{2l+3}}\cdot\frac{\{\Gamma(l+2)\}^2}{\Gamma(2l+3)}\cdot$$

$$\sum_{n=0}^{\infty}\frac{1}{(n+1)^{2l+2}}[(-1)^{n-1}N+M]F\left(l+2, l+2; 2l+3; -\left(\frac{2k}{a(n+1)}\right)^2\right)$$

$$\ldots (30)$$

A similar substitution in eq. (10) but now with μ, ν and λ as $\mu = \nu = l+1/2$ and $\lambda = 0$ gives

$$\eta_{l-1}-\eta_{l+1} = -\frac{(l+1/2)2^{2l+3}k^{2l-1}}{a^{2l+1}}\cdot\frac{\{\Gamma(l+1)\}^2}{\Gamma(2l+2)}\cdot$$

$$\sum_{n=0}^{\infty}\frac{1}{(n+1)^{2l}}[M+(-1)^{n-1}N]F\left(l+1, l+1; 2l+2; -\left(\frac{2k}{a(n+1)}\right)^2\right)$$

$$\ldots (31)$$

If in eq. (31) we put $l = 1$ and expand the hypergeometric function therein, it can be seen that the resulting expression will be the same as obtained from the sum of $\eta_0 - \eta_1$ and $\eta_1 - \eta_2$ from eq. (30). Thus as earlier eqs. (30) and (31) lead to the same approximate expression for phase shifts.

3. Conclusion

The phase shift and the scattering cross section at any energy might be found (for example : Munn *et al* 1964) by numerically solving the differential equation for each value of l provided a suitable potential energy $V(r)$ is known. But unfortunately such a solution would require tedious numerical calculations, and would not yet give any analytical form. Under this condition the approximate method as is used in the present investigation would be more appropriate.

The present method is particularly useful in the study of low energy scattering, where at most two or three values of l are important. In case othe energy is so low that only the s-state ($l = 0$) is involved, all the phase shifts except η_0 are negligible. The mormulas for scattering amplitude and the total cross section then become (Powell & Crasemann 1961)

$$f(\theta) = \frac{1}{k} \exp(i\eta_0)\sin \eta_0 \qquad \ldots \quad (61)$$

and

$$\sigma_0 = \frac{4\pi}{k^2} \sin^2 \eta_0 \qquad \ldots \quad (62)$$

respectively.

Acknowledgement

The authors wish to record their indebtedness to Professor H. N. Bose and Professor A. K. Gayen for many kindnesses and for their continued interest in the work.

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